J. Am. Chem. Soc. **1991**, *113*, 1054-1055

Homogeneous Catalytic Carbonylation of Nitroaromatics. 2. Characterization of Two Intermediates, $Ru[C(O)N(Ar)O][Ph_2P(CH_2)_2PPh_2](CO)_2$ and $Ru[C(O)OCH_3]_2[Ph_2P(CH_2)_2PPh_2](CO)_2$, and Evidence for the Carbamate-Forming Step

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Received October 5, 1990

Despite the interest in using the direct, catalytic carbonylation of nitroaromatics to carbamates (eq 1),[1-7] remarkably few details have been established about the catalytic mechanism.[3,8-14] In this communication we describe new results that allow us to propose a rough outline of the mechanism of catalysis using the mononuclear complex $Ru(dppe)(CO)_3$ [dppe = 1,2-bis(diphenylphosphino)ethane].

$$ArNO_2 + 3CO + CH_3OH \rightarrow ArNHC(O)OCH_3 + 2CO_2 \quad (1)$$

The first observable intermediate in the room temperature reaction of $Ru(dppe)(CO)_3$ with $ArNO_2$ or ArNO (where Ar = *o*-tolyl, *p*-chlorophenyl, or 2,5-dimethylphenyl) had the formula $[Ru(dppe)(CO)_3(ArNO)]$. The ^1H NMR spectrum confirmed the one-to-one stoichiometry, a fact further verified by fast atom bombardment mass spectrometry and elemental analyses. Infrared spectroscopy in the ν_{CO} region showed two absorptions of equal intensity at 2047 and 1972 cm^{-1} along with an absorption of medium intensity at 1611 cm^{-1} (Ar = *o*-methyl). NMR spectral data were consistent with, but unable to differentiate between, structures **1a** and **1b**.[15] The X-ray crystallographic analysis of the compound prepared from the reaction of nitroso-*p*-chlorobenzene and $Ru(dppe)(CO)_3$ proved that **1a** was the structure (Figure 1).[16] The formation of **1** may occur by CO insertion into the N-Ru bond of an η^2-ONAr ligand. Related insertions of electron-deficient alkynes into the Pt-N bond of $(Ph_3P)_2Pt(\eta^2\text{-}ONAr)$ have been reported.[17]

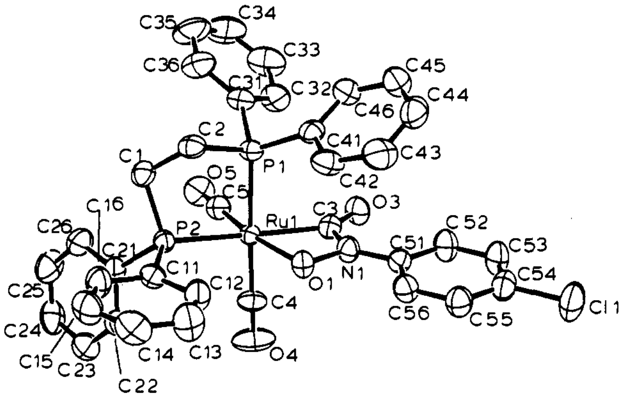
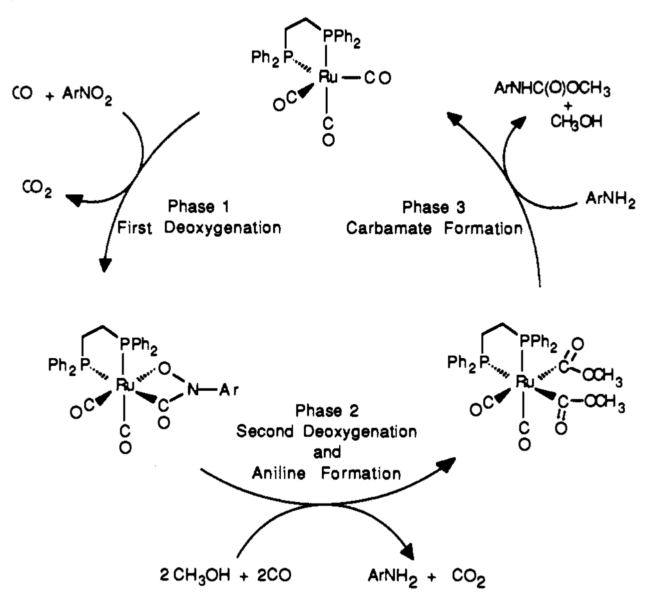
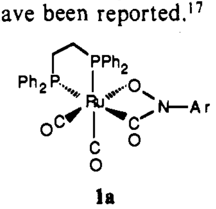


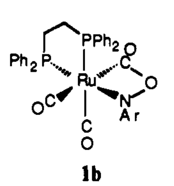
Figure 1. Molecular structure of $Ru[C(O)N(p\text{-}ClC_6H_4)O](dppe)(CO)_2$ showing atomic labeling scheme. The thermal ellipsoids are shown at the 50% level. Selected bond distances (Å): Ru1–C3, 2.081 (5); C3–N1, 1.353 (7); N1–C51, 1.388 (7); N1–O1, 1.414 (5); O1–Ru1, 2.104 (5); C3–O3, 1.239 (6). Selected bond angles (deg): O1–Ru1–C3, 64.9 (2); Ru1–C3–N1, 94.7 (3); C3–N1–O1, 108.6 (4); N1–O1–Ru1, 91.8 (3).

Scheme I





1a



1b

The complex **1** (Ar = *o*-tolyl) was stable for days at room temperature in aprotic solvents with or without CO present. Addition of methanol to solutions of **1** under CO resulted in complete reaction at 25 °C within 3 days; however, at 65 °C the disappearance of **1** was complete in 4 h. The products of the reaction were *o*-toluidene (85%), CO_2, $Ru(dppe)(CO)_3$ (40%), and a new complex (50%) which contained no NAr group. *Only*

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[15] Data for **1** (Ar = *o*-tolyl): ^1H NMR (ppm, CD_2Cl_2) 2.31 (s, CH_3), 2.48 (m, CH_2), 2.83 (m, CH_2), 6.14 (d, J_{56} = 7.8 Hz, H6), 6.74 (t, $J_{56,45}$ = 7.5 Hz, H5), 6.85 (t, $J_{45,34}$ = 7.4 Hz, H4), 6.98 (d, J_{34} = 7.4 Hz, H3), 7.19–8.18 (PPh); ^{31}P NMR (ppm, CD_2Cl_2, referenced to 85% H_3PO_4) 46.7 (d, J_{PP} = 12.3 Hz), 47.1 (d, J_{PP} = 12.6 Hz); ^{13}C NMR (ppm, CD_2Cl_2) 19.7 (s, CH_3), 26.67 (dd, J_{CP1} = 19.6 Hz, J_{CP2} = 29 Hz, CH_2), 28.12 (dd, J_{CP1} = 12.3 Hz, J_{CP2} = 26.8 Hz, CH_2), 123.0–142.1 (Ph), 183.58 (dd, J_{CP2} = 11.15 Hz, J_{CP1} = 82 Hz, CO), 196.60 (dd, J_{CP1} = 7.39 Hz, J_{CP2} = 97.4 Hz, CO), 196.91 (dd, J_{CP} = 5.44 Hz, J_{CP} = 13.3 Hz, CO).

[16] X-ray diffraction data for $RuC_{35}H_{28}P_2O_4NCl$: FW 725.09; ρ_{calcd} = 1.534 g/cm^{-1}; crystal system = triclinic; space group = $P\bar{1}$ (No. 2); $T = -24$ °C; a = 9.372 (5) Å, b = 10.59 (2) Å, c = 17.24 (1) Å, α = 102.0 (1)°, β = 104.40 (4)°, γ = 100.46 (9)°; V = 1572 (6) Å^3; Z = 2; μ = 7.13 cm^{-1} (empirical correction applied); radiation = Mo Kα; scan range 2θ = 0–51.9°; reflections collected = 6169, unique = 4818 with $I > 3.00\sigma(I)$; R = 0.049; R_w = 0.065.

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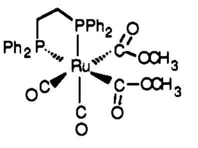
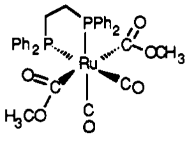
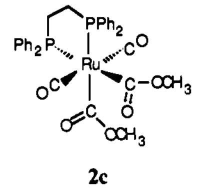
traces of carbamate were formed. Mass spectrometric data indicated that the formula of the new complex was Ru[C(O)-$OCH_3]_2$(dppe)$(CO)_2$, and spectroscopic data were consistent with the structure shown in **2a**.[18] The ^{31}P NMR spectrum displayed a pair of doublets at 46.20 and 52.42 ppm (J_{P-P} = 12.5 Hz), which is typical for an octahedral Ru^{2+} complex having inequivalent cis phosphorus atoms. The resonances of the two methoxy groups were found at 3.03 and 3.76 ppm in the ^1H NMR spectrum, and two metal carbonyl absorptions in the infrared spectrum were located at 2048 and 1998 cm^{-1}. A broad, medium-intensity absorption was found at 1622 cm^{-1} characteristic of the carbomethoxy ligand. Although the ^{13}C NMR spectrum was consistent with this structure, all of the metal-coordinated carbons were found in the same region, and no specific assignments could be made. In all of the NMR studies, evidence was found for a second isomer having a symmetric structure, **2b** or **2c**. The ratio **2a**/**2b**(**2c**) remained constant at 5/1 in all experiments.



2a



2b



2c

Complex **2** *was found to react quantitatively with o-toluidine at 95 °C over 6 h in the presence or absence of CO to form Ru(dppe)$(CO)_3$, CH_3OH, and o-$CH_3C_6H_4NHC(O)OCH_3$.* These results along with our earlier studies allow us to piece together a catalytic cycle for eq 1 (Scheme I). The species isolated may or may not prove to be the actual productive intermediates in the catalytic cycle. Additional work is in progress to address this question. The individual events occurring during phase 1 suggest the involvement of a single electron transfer from the Ru(0) complex to the nitroaromatic followed by CO_2 expulsion and CO absorption to produce **1**.[8] Phase 2 remains the "black box" of this catalytic cycle. There must be several individual chemical events operative to cleave the second N–O bond and hydrogenate the NAr group. The previously suggested intermediates (nitrene complexes, amido complexes, etc.)[8] are among the species that could be invoked to explain phase 2, but experimental evidence supporting this or any other mechanism is still needed. Whatever the nature of these reactions, the selectivity (typically 70–85%) of the catalysis {defined as [carbamate]/([aniline] + [carbamate])} may be controlled by the events in phase 2. If **2** would have been formed quantitatively from **1**, then all of the aniline produced in phase 2 would have been converted to carbamate in phase 3. As stated above, 40% of Ru(dppe)$(CO)_3$ was regenerated in the stoichiometric reaction of **1** with methanol without formation of carbamate. Combining the knowledge of the selectivity of phase 2 with the higher activation barrier of phase 3 allowed us to design a high-yield synthesis of **2**. Three equivalents of *o*-nitrotoluene reacted with Ru(dppe)$(CO)_3$ in a methanol/toluene solution (1/9) under CO (2 atm) at 60–70 °C for 2 h, producing **2** in 95% yield. In phase 3, the formation of carbamate probably occurs via the nucleophilic attack of aniline on **2**. Expulsion of carbamate and methanol to regenerate Ru(dppe)$(CO)_3$ could occur by a few straightforward chemical reactions.

While Scheme I explains the qualitative features observed in the catalysis, additional research is required to elucidate the individual steps, especially in phase 2, and to put the entire mechanism on a more quantitative foundation.

Acknowledgment. This research was supported by a grant from the National Science Foundation (CHE-8714326). We gratefully acknowledge valuable discussions with John Grate and David Hamm.

Supplementary Material Available: Tables of crystallographic data, atomic positional and thermal parameters, and bond distances and angles for $RuC_{35}H_{28}P_2O_4NCl$ (14 pages); listing of observed and calculated structure factors for $RuC_{35}H_{28}P_2O_4NCl$ (33 pages). Ordering information is given on any current masthead page.

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[18] Data for **2**: ^1H NMR (ppm, C_6D_6) 2.22 (m, CH_2), 2.90 (m, CH_2), 3.71 [s, OCH_3 of **2b**(**2c**)]; ^{13}C NMR (ppm, C_6D_6) 27.0 (dd, J_{CP1} = 12.9 Hz, J_{CP2} = 25.1 Hz, CH_2), 48.94 (s, CH_3), 50.17 (s, CH_3), 120.2–134.6 (Ph), 195.4 (dd, J_{CP1} = 12.11 Hz, J_{CP2} = 89.5 Hz, CO), 197.8 (dd, J_{CP1} = 9.11 Hz, J_{CP2} = 89.3 Hz, CO), 197.77 (J_{CP1} = 10.58 Hz, J_{CP2} = 6.4 Hz, CO), 199.64 (t, $J_{CP1,CP2}$ = 12.5 Hz, CO); ^{31}P NMR [ppm, C_6D_6, referenced to 85% H_3PO_4) 43.7 (s, **2b**(**2c**)]; FABMS, P (*m/e*) 678.

Ring Opening Induced by Iminyl Radicals Derived from Cyclobutanones: New Aspects of Tin Hydride Cleavage of *S*-Phenyl Sulphenylimines

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Received September 17, 1990

Despite the dramatic surge in the application of radical reactions to organic synthesis,[1] the synthetic potential of iminyl radicals has hardly been exploited. The main limiting factor has been the lack of a convenient and general method for generating these species.[2] We have recently described[3] a mild and practical process for producing iminyls from *S*-aryl sulphenylimines using tributylstannane, which we applied to the synthesis of various Δ^1-pyrrolines derivatives. We have now found that this reaction could be used to induce ring opening of cyclobutanones via the corresponding cyclobutylimino radical.

The few kinetic studies of the β-scission of iminyl radicals[4] as well as scattered examples involving fragmentation of cycloalkyliminyl intermediates[2a,b,5] indicated that, for cyclobutyl derivatives, this process could be sufficiently rapid to compete favorably with premature quenching by the stannane. Indeed, slow addition (ca. 5 h) of *n*-Bu_3SnH in cyclohexane to a refluxing solution of sulphenylimine **3a**[6] in the same solvent (in the presence

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